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Formation and Removal of Halogenated Hydrocarbons in Drinking Water A Case Study at Huron, South Dakota

South Dakota School of Mines and Technology
Rapid City

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A CASE STUDY AT HURON, SOUTH DAKOTA

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A Case Study at Huron, South Dakota

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16. ABSTRACT

During the past few years, over 180 organic chemicals have been identified in drinking water across the United States. A group of these compounds known as trihalomethanes, are formed when chlorine reacts with organic substances found naturally in most surface waters. A nation-wide EPA study of 80 cities in 1975 found that Huron, South Dakota's drinking water had one of the highest concentrations of trihalomethanes encountered. This project was funded in an effort to assist Huron with its problem.

Samples were collected from the water treatment process at Huron. These samples were tested for the same six organic compounds used by EPA in the 1975 survey. High levels of chloroform and bromodichloromethane were found to be formed during the treatment process. The haloform reaction was found to be very pH dependent and changing the point of application of the prechlorine dose reduced chloroform in the effluent by 75%. Total haloforms in the drinking water could be lowered further if the effluent pH could be lowered to a near neutral pH. Additional aftergrowth of the chlorinated hydrocarbons occurred in the distribution system.

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FORWARD

One of the many challenges facing communities and the Environmental Protection Agency is to assure the provision of safe drinking water. This task is complicated by the variety of contaminants entering our water sources. During the past few years, over 180 organic chemicals have been identified in drinking water across the United States. A group of these compounds known as the trihalomethanes, are formed when chlorine reacts with organic substances found naturally in most surface waters. This is of concern since chlorine is the principal disinfectant used for treating drinking water. A nation-wide EPA study of 80 cities in 1975 revealed that Huron, South Dakota's drinking water had one of the highest concentrations of trihalomethanes encountered.

In an effort to assist the community with this problem, we funded the project described by this report. As a result of the study, the trihalomethane concentration in the Huron water supply was greatly reduced. Also, this research has helped to expand our knowledge on the formation of trihalomethanes and the techniques to reduce their concentrations in drinking water.

We express our appreciation to the South Dakota School of Mines, the City of Huron and the South Dakota Department of Environmental Protection for their cooperation and assistance with the project.

John A. Green
Regional Administrator

ABSTRACT

Samples were collected from the water treatment process at Huron, South Dakota. These samples were tested for the same six organic compounds used by EPA in a recent survey of drinking waters.

High levels of chloroform and bromodichloromethane were found to be formed during the treatment process. The haloform reaction was found to be very pH dependent and changing the point of application of the prechlorine dose reduced chloroform in the effluent by 75%.

Total haloforms in the drinking water could be lowered further if the effluent pH could be lowered to a near neutral pH. Additional aftergrowth of the chlorinated hydrocarbons occurred in the distribution system.

This report was submitted in fulfillment of Grant No. R008128010 by the South Dakota School of Mines and Technology under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from August 15, 1975 to August 15, 1976 and work was completed as of January 31, 1977.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

EPA	-- United States Environmental Protection Agency
MGD	-- Million gallons per day
ppm	-- part per million
ppb	-- part per billion
GC	-- Gas Chromatograph
MS	-- Mass Spectrophotometer
GAC	-- Granular Activated Carbon

SYMBOLS

$CHCl_3$	-- Chloroform
$CHCl_2Br$	-- Bromodichloromethane
µg/l	-- microgram per liter

ACKNOWLEDGEMENTS

The interest and cooperation given by the administrative officials of Huron, South Dakota is gratefully acknowledged. We would particularly wish to express our thanks to the Huron City Council; Mr. Glenn Housiaux, City Engineer; and Mr. Harold Root, Water Treatment Plant Superintendent.

Technical assistance with the instrumentation was given by Dr. A. A. Stevens of the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Bacteriological testing was conducted in the laboratories of the South Dakota Department of Environmental Protection.

SECTION 1

INTRODUCTION

General

Within the last three years, public attention has again focused on the water it consumes as being a possible health hazard. The scrutiny given to the New Orleans public water supply by the national media is an example of this attention. With cancer as a major cause of death in the United States, it is not easy to disregard the small concentrations of the many compounds which may be present in drinking water supplies.

In an attempt to gain some indication as to the magnitude of the problem, EPA conducted an 80 city survey in which the raw and treated drinking waters were examined for six organic compounds. The six organic compounds selected were the four trihalomethanes; chloroform, bromodichloromethane, dibromochloromethane, and bromoform; as well as 1, 2 - dichloroethane and carbon tetrachloride. The concentrations of these compounds ranged from zero to trace amounts in the raw waters, but they were wide-spread in the finished waters. Results of the survey indicate that the formation of these compounds is caused by the chlorination practices normally followed during water treatment operations (1).

Results of the survey (1) showed that chloroform was detected in the finished water of 100% of the cities surveyed, and that bromodichloroethane was found in 97.5% of the finished waters. Huron, South Dakota had the dubious distinction of having the highest concentration of bromodichloromethane (116 µg/1) as well as the second highest concentration of chloroform (309 µg/1 compared to a high value of 311 µg/1).

Although a definite correlation between the rate of human cancer and the concentrations of the organics in the drinking water did not exist, it was thought to be prudent to reduce these concentrations as much as possible. Consequently a study was carried out at the Huron Water Treatment Plant and the results are reported herein.

Objectives

The objectives of the study were:

(1) To qualitatively and quantitatively analyze the Huron water supply to more precisely define the problem of contamination by chloroform and other related halogenated hydrocarbons.
(2) To establish the source of these compounds.
(3) To find a means of water treatment which would effectively reduce the concentrations of these compounds.

Scope of Work

All the field work was conducted in the City of Huron, South Dakota. Samples were collected from the on-line facility which serves the citizens of Huron. Samples were not taken from pilot plant facilities or other microscale operations.

Initial monitoring of the plant operations began in February, 1976. Modifications to the treatment scheme were tried on an experimental basis in March, and some permanent changes were implemented in late April, 1976. From May until August, 1976, extensive sampling was conducted to determine the effects of in-plant modifications. Additional bench-scale experiments were also carried out at this time.

Analytical work was performed on campus at the South Dakota School of Mines and Technology laboratories. Some initial field measurements were made on the samples in the laboratory at the Huron Municipal Water Treatment Plant.

SECTION 2

CONCLUSIONS

The investigation at Huron has provided valuable insight into the formation of haloforms under actual water treatment practices. The following conclusions were drawn from the study:

1. The haloforms form during and after water treatment. They were found to form in high concentrations at the point of chlorination and lime addition.

2. The potential chloroform concentration at Huron remains high, in the range of 200 to 325 ppb. However, the relocation of the pre-chlorination dose to a point following re-carbonation resulted in a significant reduction in the chloroform concentration.

3. The mechanism of chloroform formation is strongly pH dependent, and the chloroform concentration in the clear well closely follows the effluent pH.

4. Lowering of the effluent pH below 9 is limited by problems of water stability.

5. Haloform concentrations continue to rise after entering the distribution system.

6. The ultimate solution to the problem of haloform formation is precursor removal, but a more practical solution is to prevent their formation during the treatment process.

7. The mechanism of bromodichloromethane formation does not appear to be strongly pH dependent.

SECTION 3

RECOMMENDATIONS

Recommendations which evolved from the study are:

1. The disinfection should continue at the revised location.

2. Additional data on bromodichloromethane formation should be gathered. This constituent was not significantly reduced in this study.

3. Additional work should be done on the aftergrowth of haloforms within the distribution system.

4. Identification of the precursor source(s) should be considered in an attempt to reduce the potential for chlorinated hydrocarbon formation. Possibilities to be evaluated should include:

    a. point sources upstream

    b. the local practice of disposing of dead animals in the stream

    c. precursor increase from biological growth in stagnant water

    d. agricultural runoff as a precursor source

5. Alternate methods of disinfection should be considered such as the use of ozone, chloramines and chlorine dioxide.

SECTION 4

BACKGROUND LITERATURE

The National Organics Reconnaissance Survey (NORS) was conducted by EPA in late 1974 and the spring of 1975 (3). The objectives of the survey were to monitor the concentrations of four specific trihalomethanes, to determine the effects of raw water sources and water renovation practices on the formation of these compounds and to determine the organic content of the drinking water supplied to cities in different parts of the U.S. From this survey came several conclusions. These conclusions dealt with relationships of nonvolatile total organic carbon and trihalomethane concentrations, the occurrence of trihalomethanes in precipitation softening treatment plants, relationships of chlorine residual and trihalomethane concentrations and correlations between the use of ozonation, powdered activated carbon, granular activated carbon and lower trihalomethane concentrations. One of the study's major conclusions was that the four halomethanes were "widespread in chlorinated drinking waters in the U.S. and result from chlorination."

The work of J. J. Rook and Bellar, Lichtenberg and Kroner innovates the mechanics of haloform reactions (4),(5). The major emphasis of the work by Rook deals with the type of organic precursors that contribute to haloform formation, such as meta-hydroxy aromatics as well as dihydroxy chlohexane, the conditions favorable to haloform formation, precursor removal by macroreticular resin adsorption, chlorination combined with ozonation and removal of halogenated organics by activated carbon adsorption and air stripping (4).

The work of Bellar, Lichtenberg and Kroner includes a condensed overlook of a GC-MS method for the identification of volatile organics and conclusions based on their research in this field of study. Possible contamination by lab chloroform of water samples to be tested for haloforms, the results of surface and other water supplies monitoring and some of the chlorinating procedures used in treatment plants that contribute to haloform concentrations are some of the conclusions discussed (5).

An extensive overlook of different types of methods for the determination of the organic substances in water supplies that give rise to such characteristics as color, odor and taste was published in a 1967 edition of the ASCE Journal (6). The methods reviewed include adsorption onto carbon, liquid-liquid extraction counter-current extraction, freeze concentration, distillation, visual range spectroscopy, infrared spectroscopy, ultraviolet spectroscopy, mass spectroscopy, gas-liquid chromatography, paper chromatography, thin-layer chromatography and the use of a carbon analyzer.

A more recent analytical method for the isolation and determination of volatile organics in drinking water is offered by Bellar and Lichtenberg (7). A combination of gas-Chromatography, mass-spectrometry is described including an extensive depicture of the types of materials used in the analysis. Simplified, the procedure consists of adsorption onto a solid sorbent and the separation and detection of the concentrations of the volatile organics.

Another, newer method of gas chromatographic analysis uses acetylated XAD-2 resins, pyridine and a small pre-column of copper (II) chloride (8). This procedure makes it possible to get better detection limits and shows better resolution into haloform peaks than previous methods.

In a March 1975 report, Morris and McKay (9) reviewed the mechanics of the formation of halogenated organics in water supply. The principal points in this study are: ways chlorinated organics are introduced into the water supply, the haloform reaction, the precursors to haloform formation and several treatment modifications to reduce haloform concentrations.

The authors cite four principal routes for chlorinated organics to enter into water supply. These four methods are non-point sources, industrial discharges, chlorination of sewage or industrial wastewater and the chlorination of organic matter in drinking water. Some of the chlorine-containing compounds (found in water supplies) consist of fungicides, pesticides, polychlorinated biphenyls, and haloforms.

Haloform reactions, according to the authors, usually take place in an aqueous, alkaline solution. The types of substances most likely to react to form a haloform are organic compounds with an acetyl group or compounds with a group easily oxidized to an acetyl group, such as acetaldehyde and ethanol. A sequence of seven reactions take place to form a haloform. The first of these reactions, and the slowest, is the initial dissociationof a positively charged hydrogen to yield a carbanion. The following reactions leading to the end-product of a haloform all proceed at essentially the same speed.

The precursors to haloform reactions in natural, unpolluted waters stem from organic matter whose source is plant life. High, molecular weight humic substances, such as fulvic acids, contribute to the chlorine demand of the water. The high, chlorine demand of water has been linked with significant haloform concentrations. Low, molecular weight carboxylic acids are common in water supply in the several milligram per liter range. The more complex carboxylic acids yield to hypochlorite reactions forming haloforms. The simple, aliphatic monocarboxylic acids are relatively nonreacting with hypochlorite.

Two approaches to the control of haloform concentrations in drinking water supplies are emphasized. The first method is the removal of as much of the precursor as possible, the second is to remove the byproducts of chlorination after they are formed. The techniques for accomplishing the first method are: the discontinuation of prechlorination, storage of water for several months, coagulation-filtration, ozonation, potassium permanganate treatment or combinations of these. Procedures for the second approach include adsorption onto activated carbon and aeration techniques (9).

Bench-scale and pilot plant operations dealing with granular activated carbon filters and ozonation for the control of trihalomethanes are some of the main points in an EPA report (10). Briefly, the pilot plant studies consist of the removal of trihalomethanes from treated tap water with GAC filters, and filtration by GAC filters after conventional pretreatment which was subsequently followed by chlorination, or chlorination and ozonation. The principal trihalomethanes tested for were chloroform, bromodichloromethane, dibromochloromethane and bromoform.

In the first pilot plant experiment, coal-base and lignite-base GAC filters were tested over specific time periods for the percentage reduction of chloroform and bromodichloromethane. Tap water from Cincinnati, Ohio was applied with the chloroform range from 34-72 µg/l and the bromodichloromethane range of 8-20 µg/l concentrations. After 4 weeks, the coal-base GAC filter showed about a 40% chloroform removal, whereas the lignite-base showed approximately an 80% removal. Similar results were obtained for bromodichloromethane. Because the two carbons were subjected to different loadings, it can not be definitely stated that the lignite-base GAC is superior. However, the researchers did conclude that: "The trend of the data from the lignite-base GAC would indicate that its ability to remove chloroform was somewhat greater than the coal-base material" (10).

In the next study, Ohio River water was coagulated, settled and then filtered by one of three different methods, and finally chlorinated or chlorinated and ozonated. The types of filters used were (a) dual media (sand/coal), (b) coal-base GAC, (c) dual media followed by coal-base GAC. Summarizing the results, ozo-

nation and chlorination of the effluents from filter No. 1 actually caused an increase in the chloroform concentration, but a decrease in the bromodichloromethane over a 6 day period. However, the same treatment of effluents from filters No. 2 and 3 did not substantially affect the amount of chloroform, bromodichloromethane or dibromochloromethane over a 6 day period. The total range of the concentrations of the trihalomethanes in this specific experiment were from .2 to 15 µg/l, and no bromoform was found in any of the samples tested.

Also, from this study came several conclusions based on chlorination of raw and different types of treated water from the Ohio river. The first of these conclusions states that when enough chlorine is added to satisfy the chlorine demand of the raw water, seven times the amount of chloroform is formed then when filtered effluent of a dual media filter is chlorinated. When the water was filtered on a fresh coal-base GAC filter and chlorinated, only one-eightieth of the amount of chloroform was formed. Secondly, chloroform has been found to have the most significant concentration in the water samples, followed by bromodichloromethane and dibromochloromethane in the ratio of 100:15:1. Thirdly, the water samples tested with the higher chlorine demand had the highest trihalomethane concentrations. It was concluded, furthermore, that both inorganic and organic chlorination byproducts were formed, since it was discovered that only 3% of the chlorine added went into the trihalomethanes. Lastly, it was found that as long as there was a chlorine residual measured, there was a trihalomethane concentration (10).

A recently published study measured halogenated methanes in Iowa finished waters. Concentrations of the haloforms were compared with turbidity values for some samples. A correlation between river turbidity and chloroform seemed to be indicated. Minimum recorded values of 45 and 55 µg/l chloroform occurred at low flow conditions while the high of 230 µg/l chloroform was recorded at the highest turbidity. The authors concluded that: "the upper Midwest agricultural belt is the major upstream contributor of halogenatable organic runoff to the Mississippi River system and that all downstream users are affected by this non-point source discharge" (11).

At this point in time, no one presumes to have all the answers which are necessary to be certain that the organics problem in drinking water is under control. EPA has set this tone in a July issue of the Federal Register in which they discussed the options available for the control of organic contaminanants (12). They expressed concern for the possible health hazard created by these compounds, and invited public comment regarding the regulatory questions discussed.

Current thinking on treatment modifications to control the

trihalomethanes is given in a recent document released by EPA (13). The discussion includes precursor removal by the use of granular activated carbon and the prevention of chloroform formation by using alternate means of disinfection. A main disadvantage to the use of carbon beds is the limited time before the adsorption capacity of the carbon is expended. Alternate disinfectants such as ozone, chlorine dioxide, and chloramines are being considered. All the methods have both advantages and disadvantages. Work is currently underway to further define when these methods are applicable.

Water treatment at Huron, South Dakota is described in detail in the next section. The water treatment process employs lime softening so the chlorination occurred at a high pH level. The quality of the raw water is quite variable, and the presence of organics has been a frequent problem. A very recent study, published after the work reported herein was concluded, addresses this combination of variable water quality and high pH (14). Stevens and his EPA coworkers used bench and pilot-scale projects to investigate the effects of precursor concentrations, pH, type of disinfectant and temperature on trihalomethane formation. The results obtained at the full-scale treatment plant at Huron confirm some of the conclusions Stevens et al drew from their bench scale studies, specifically regarding the importance of the point of location of chlorination in the treatment process, and the additional trihalomethane produced at the higher pH levels.

SECTION 5

HURON SOUTH DAKOTA MUNICIPAL WATER TREATMENT PLANT

General

Huron's municipal water supply is the James River, a small slow-moving stream which flows through eastern South Dakota. The water quality is extremely variable as shown in Table 1. Agricultural runoff, upstream wastewater discharges, dead animals disposed in the stream, and seasonal variations all combine to make the raw water difficult to treat for domestic use. According to the operator's log at the treatment plant, the river water pH usually falls within a range of from 7.5 to 8.5.

TABLE 1. JAMES RIVER WATER QUALITY (2).

Constituent	Raw Water		
	Low	High	Average
Total solids, ppm	271	2180	547
Total hardness, ppm	131	963	256
Iron, ppm	0.02	0.05	-
Calcium, ppm	53	158	-
Chloride, ppm	51	157	-
Sulphates, ppm	100	785	167
Bicarbonates, ppm	98	812	248
Fluorides, ppm	0.3	0.4	-
Nitrates, ppm NO_3	0.3	2.0	-
Magnesium, ppm	33	119	-
Sodium, ppm	29	352	80
Potassium, ppm	14	25	-

Treatment

Water treatment at Huron consists of chemical addition, sedimentation, flocculation, clarification, recarbonation, filtration and chlorination. A process schematic is shown in Figure 1. A more detailed process description follows:

Process step	Description
River to plant	Raw water is pumped from an intake located about 100' upstream from a small dam.
Initial chemical addition	Rapid dispersion of potassium permanganate, activated carbon alum, and a polyelectrolyte (Nalco 607).
Presedimentation	Settling of about 1 hour duration at a flow of 6 MGD.
Prechlorination	Initial chlorine dose, approximately 6 to 7 mg/l. Point of application revised during study period.
Rapid Mix No. 1	Chemical dispersion of lime, soda ash (occasionally), and sodium aluminate (Nalco 617).
Flocculation	Gentle stirring of the water-chemical mixture. Detention time at 6 MGD is about 1.5 hours.
Clarification	Settling of slightly more than 2 hours at a flow of 6 MGD.
Recarbonation	Adjustment of pH with CO_2 to obtain a stable water. Fluoride for the control of dental caries and polyphosphate (Nalco 918) are added at this basin. The prechlorination dose was moved to this location in late April 1976.
Gravity filters	Filtration process using antrafilt media.
Postchlorination	A final chlorine dose for disinfection.

Process step	Description
Clearwell storage	Short term water storage at the treatment plant.

Chemical feed rates vary from day to day depending upon the initial water quality and the plant operation. Average daily use values of from 1 to 3 MGD are common with peak day demands approaching 7 MGD having been recorded. Chemical feed rates for 9/8/75 are shown below in Table 2. Flow on this date was about 2.5 MGD.

TABLE 2. CHEMICAL FEED RATES FOR SEPTEMBER 8, 1975

Chemical	Feed Rate, mg/l
Prechlorine dose	6.8
Postchlorine dose	2.6
Carbon	2.2
Soda ash	0
Lime	152
Alum	29
Sodium Aluminate (Nalco 617)	9.6
Fluoride	1.2
Stabilizer (Nalco 918)	2.0
Potassium permanganate	0.98
Polyelectrolyte (Nalco 607)	0.80
Carbon dioxide	36

SECTION 6

METHODS

Field

In order to locate the source(s) of formation of the haloforms, a series of seven sampling sites closely tracing the progress of water treatment at the Huron plant were selected. These sampling locations are indicated by station number on Figure 1. They are:

Station 1 - Raw water intake to the treatment plant.
Station 2 - Effluent from presedimentation tank.
Station 3 - Effluent from rapid mixer.
Station 4 - Effluent from flocculation tank.
Station 5 - Effluent from sedimentation tank.
Station 6 - Above gravity filters.
Station 7 - Clear well.

Once the sites were chosen and the sampling procedures established, the samples were collected by Mr. Larry Doss, our field engineer in Huron. The samples were collected and sealed bubble free in 60 ml glass bottles, packed in ice, and sent by air express to the laboratory. On arrival at the laboratory, the samples were stored in a refrigerator at about 5°C until analyzed, normally on the following day.

It should be noted that no reducing agent was added to the samples to stop the action of chlorine and the corresponding formation of haloforms. While there may be some disadvantages in allowing the reaction to proceed, this does allow for establishing which stage(s) of the treatment process have conditions favorable for haloform formation. By allowing the reaction to proceed for a minimum of 24 hours the results give an indication of the potential haloform concentration under the existing conditions. Packing the samples in ice protected them from temperature extremes during shipment. While it was difficult to precisely control the time between sample collection and analysis, results of previous work suggested little or no increase in haloform concentration after 15 hours of contact with chlorine (5). It might also be noted that the sample handling procedures are in close agreement with those used in the National Organics Reconnaissance Survey (3).

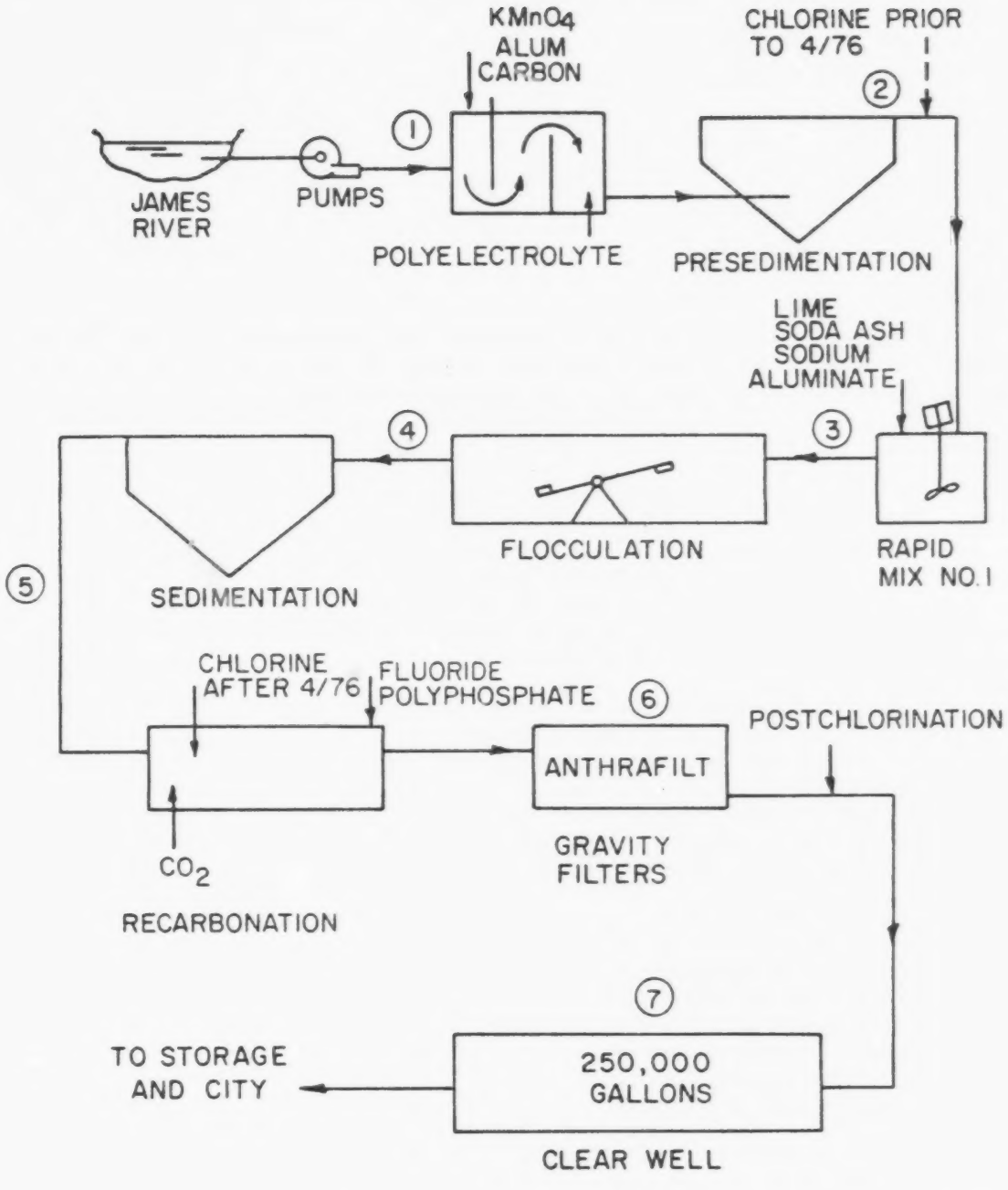


Figure 1. Process flow diagram for water treatment.

Laboratory

Apparatus

The basic apparatus used in this study consisted of a Varian Model 705 Gas Chromatograph fitted with a modified inlet system, a Tracor Model 310 Hall Electrolytic Conductivity Detector, and a Varian Model A-25 strip chart recorder. Additional apparatus included a purging device, trap, and desorber system, all of which were constructed after those described by Bellar and Lichtenberg (7). The trap was constructed with an appropriate fitting to enable it to be coupled directly to the injection port of the G.C. Thus, the injection port heater of the G.C. served as the heat source for desorption, and the regular carrier gas flow served to sweep the desorbed gases onto the column. A separate helium gas line and flow control valve were installed for backflushing (desorbing) the trap.

The various instrumental parameters used in the study follow.

Instrumental Parameters

Purging Device
- Purging Gas - - - - - - - - - - - - - - He, 20 ml/min
- Trap (1/8" x 20 cm - - - - - - - Packed with 60-80 mesh Tenax GC

Desorption
- Desorption Gas- - - - - - - - - - - - He, 20 ml/min
- Trap Temp. - - - - - - - - - - - - - - - - - 180° C
- Column Temp.- - - - - - - - - - - - - - - - - 30° C

Gas Chromatograph
- Column
  - Construction - - - - 6mm x 10 ft glass column
  - Packing - - - - - - - - 60/80 mesh Tenax GC
- Carrier Gas - - - - - - - - - - - - - - He, 20 ml/min
- Temperature Program
  - Preisothermal hold - - - - - 14 min at 95° C
  - Program - - - - - - - - - - - 8°/min to 180° C
  - Transfer line (glass lined)- - - - - - 200° C
- Detector
  - Electrolyte - - - - - - - - - - - - - - 1 ml/min
  - Reaction Gas - - - - - - - - - - $-H_2$, 10 ml/min
  - Furnace Temperature- - - - - - - - - - - 820° C
  - Attenuter- - - - - - - - - - - - - - - - - - 16 x
  - Conductivity - - - - - - - - - - - - - - - - 3 x
  - Recorder - - - - - - - - - - 1 mv, 0.5 cm/min

Reagents

All solutions were prepared, when possible, from reagent grade chemicals.

Organic free water was prepared by purging 5 ml of distilled water with inert gas (He) for 11 min. at 20-30 ml/min.

Stock Standard Solutions. Standards of $CHCl_3$ and $CHCl_2Br$ were prepared in methanol at 100 and 500 ppm using a 10 µl syringe and 50 ml volumetric flasks. Further dilutions with methanol were made as required. All standard solutions were refrigerated when not in use.

Working Standard Solutions. Working standards were prepared by adding the appropriate volumes of stock standards to 5 ml of purged distilled water.

Analytical Procedures

Before analyzing any samples the trap was conditioned by placing it in the inlet port of the gas chromatograph and flushing with helium at 20 ml/min and 180° C for 4 min. Following conditioning of the trap a blank and two standards were run in order to check instrument response and calibration.

Once the instrument was calibrated, the samples were analyzed as follows:

1. Place the sample bottle in a water bath at 20° C and allow the temperature to equilibrate.
2. Using a 5 cc glass hypodermic syringe, transfer 5 ml of sample to the purging device.
3. Attach the trap to the exit port of the purging device and purge the sample for 11 min with helium gas at 20 ml/min.
4. Transfer the trap to the modified inlet port of the gas chromatograph and backflush (desorb) with helium at 20 ml/min at 180° C for 4 min.
5. Replace the trap with a plug, quickly raise the column temperature to 95° C and start the recorder.
6. Following 14 min at 95° C, program the column temperature at 8° C/min to 180° C.
7. Following 5 min at 180° C, reduce the column temperature to 30° C, or less, and proceed with the next sample.

SECTION 7

RESULTS

Initial Data

Initial data to better define the location of trihalomethane formation were collected in February 1976. Samples were taken from several stations within the water treatment plant and analyzed for the six organic compounds previously discussed. These data are presented in Table 3 shown below.

TABLE 3. INITIAL DATA FOR TRIHALOMETHANE FORMATION

Date	pH	Station	$CHCl_3$, µg/l	$CHCl_2Br$, µg/l
2/10/76	8	1 (raw water)	a	a
2/23/76	8	1 (raw water)	a	a
2/10/76	7.8	2 (before pre-chlorination)	5	a
2/23/76	7.8	2 (before pre-chlorination	8	a
2/23/76	7.7	2A(between Cl_2 and lime)	145	34
2/10/76	11.5	3 (lime addition)	203	22
2/23/76	11.5	3 (lime addition)	180	13
2/10/76	11.5	4 (post-flocculation)	208	14
2/23/76	11.5	4 (post-flocculation)	175	6
2/10/76	11.5	5 (post-clarification)	215	10
2/10/76	9.6	6 (post filter)	176	35
2/10/76	9.5	7 (clear well)	210	42

a. Below detection limit of 0.1 µg/l

Samples taken on both February 10th and 23rd clearly indicate that both chloroform and bromodichloromethane form between Sta. 2 (presedimentation) and Sta. 3 (chemical addition). Conditions were optimum for trihalomethane formation. Nonsettleable precursors had not been removed, a chlorine dose had just been added, and the pH of the solution was raised. The other four compounds were not detected.

There are some additional items that should be noted regarding the data in Table 3. On both occasions, the organic compounds were not detected in the raw water, but they were formed as a result of the water treatment process. Specifically a reaction occurred between precursors and the chlorine added to the water. Initial formation of chloroform is rapid, and the concentration gradient was such that traces were detected at Sta. 2, just before the chlorine was added. The formation of bromodichloromethane did not appear to be as rapid a reaction. Once formed, the concentrations were of the same order of magnitude throughout the remainder of the treatment process. For example, the chloroform concentration was about 200 µg/l after lime was added.

Previous work has established that the haloform reaction proceeds rapidly in alkaline aqueous solutions (9). Therefore, it seemed prudent to attempt to chlorinate at lower pH levels.

Data in Table 4 reflect the trihalomethane concentrations formed when the prechlorination dose was temporarily discontinued, but while the normal post chlorination was continued. Both chloroform and bromodichloromethane concentrations were substantially reduced as seen by the concentrations recorded at Stations 5 and 6. The increase evident in samples collected from the clear well, Sta. 7, results from the relatively short time that the prechlorination step was interrupted. At this time, it was not known what changes in bacterial quality could be anticipated when the prechlorination dose was not being used. Therefore, the clear well was not adequately flushed and the water in the clear well contained a mixture of high and low level organics.

TABLE 4. TRIHALOMETHANE FORMATION WITHOUT PRECHLORINATION

Date	pH	Site	$CHCl_3$, µg/l	$CHCl_2Br$, µg/l
3/1/76	8.1	1 (raw water)	a	a
3/1/76	7.7	2 (before pre-chlorination)	a	a
3/1/76	11	3 (lime addition)	3	a
3/1/76	11.1	5 (post-clarification)	8	a
3/1/76	9	7 (clear well)	111	23
3/18/76	7.8	1 (raw water)	a	a
3/18/76	11.1	5 (post filter)	a	a
3/18/76	7.7	6 (post filter)	17	3
3/18/76	8.6	7 (clear well	73	20
3/24/76	8.1	1 (raw water)	a	a
3/24/76	11.3	3 (lime addition)	a	a
3/24/76	10.8	5 (post clarification)	a	a
3/24/76	7.6	6 (post filter)	5	0.3
3/24/76	7.4	7 (clear well	25	10

a. Below detection limit of 0.1 µg/l.

Having thus established that eliminating the prechlorination step would result in lower trihalomethane formation, it became necessary to establish what affect this procedure had on the overall water treatment process. In the Huron plant, the prechlorination step was primarily used to lengthen filter runs between washings.

It was decided to move the prechlorination dose to the recarbonation basin. This new location still allowed the chlorine to be applied prior to the filters, but after the pH had been lowered. The relocation is shown in Figure 2.

Initial results from moving the point of chlorine application are given in Table 5. Extra water samples were collected

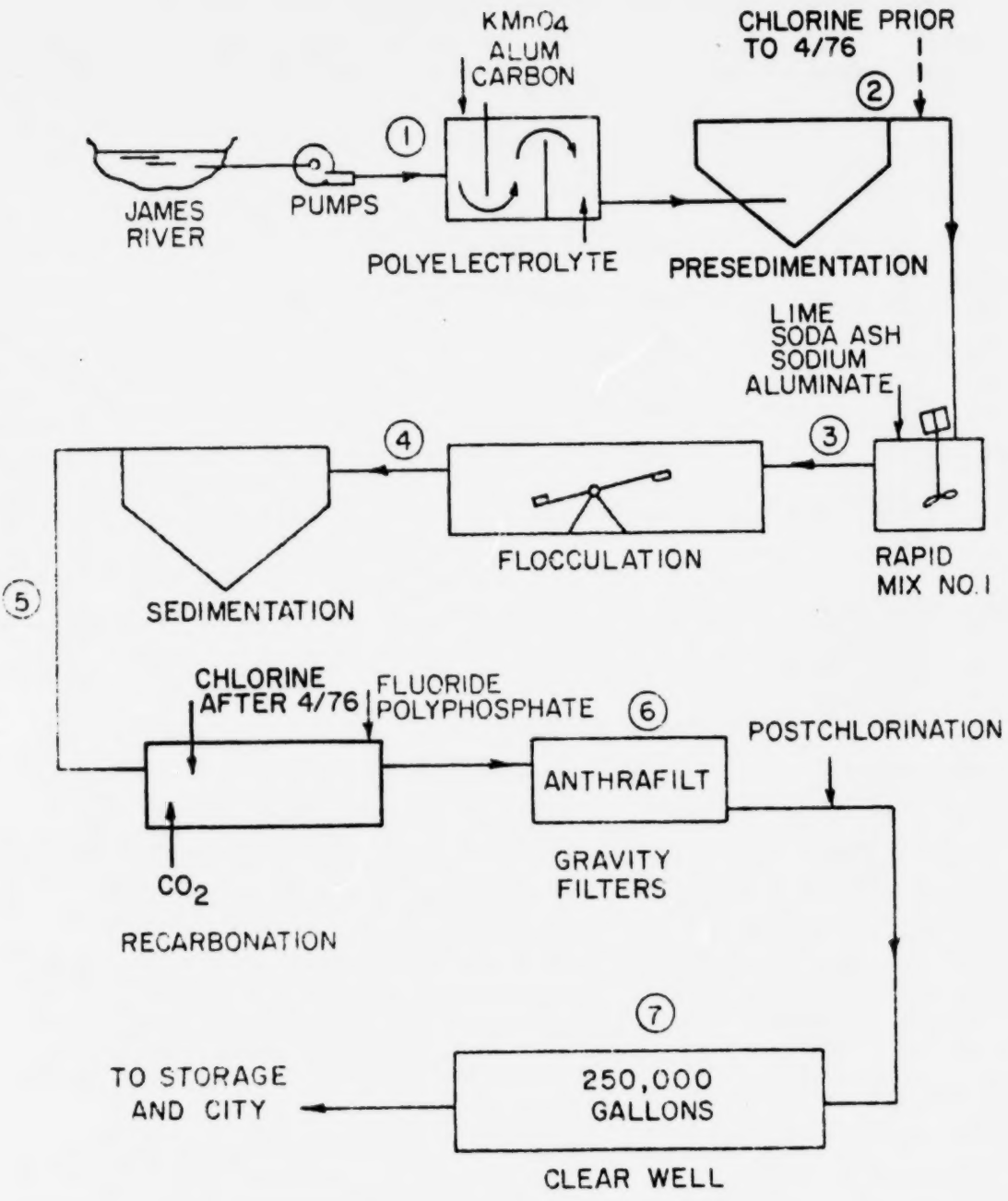
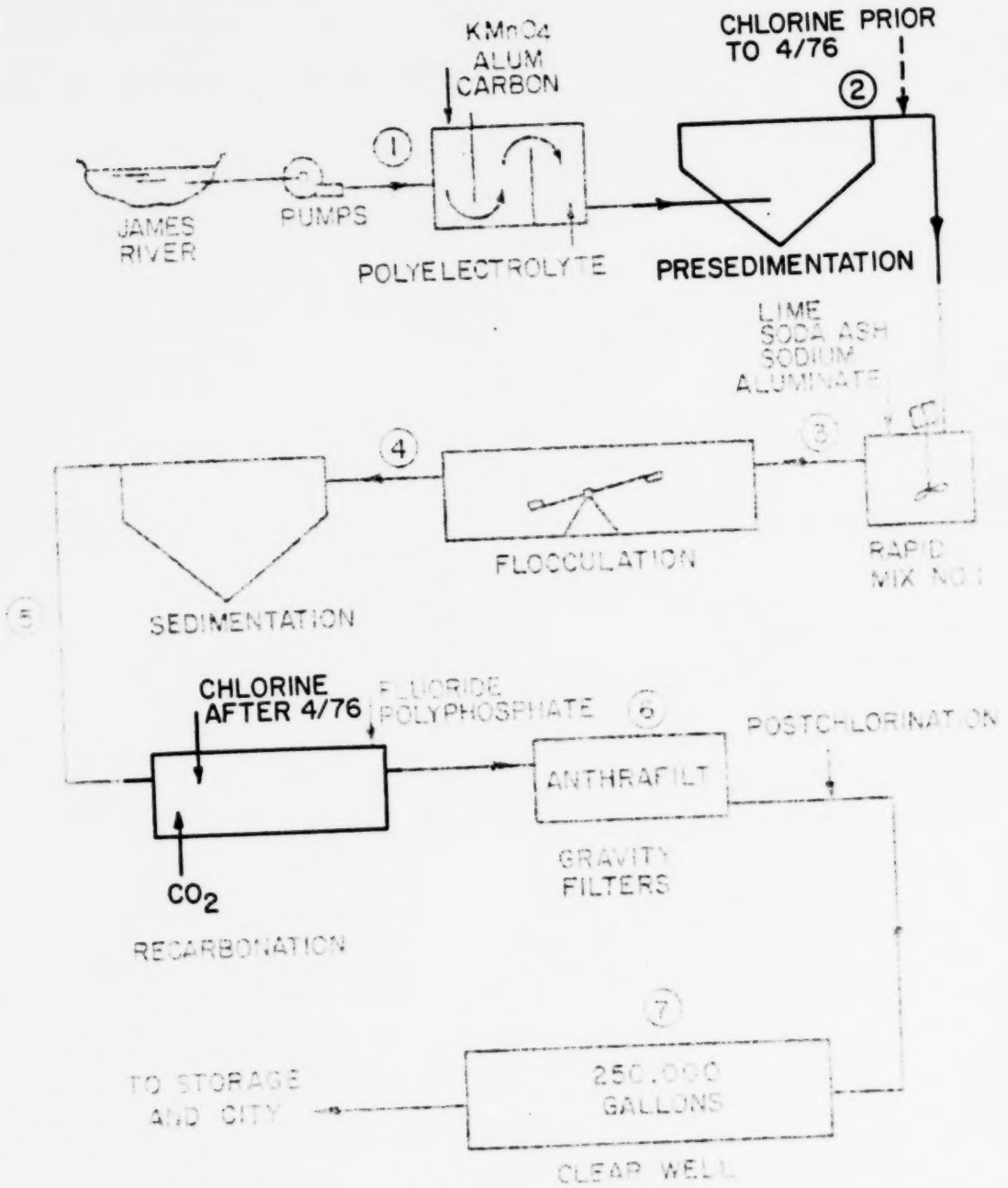


Figure 2. Relocation of prechlorination dose.


KMnO4
ALUM
CARBON
CHLORINE PRIOR
TO 4/76
1
2
JAMES
RIVER
PUMPS
POLYELECTROLYTE
PRESEDIMENTATION
LIME
SODA ASH
SODIUM
ALUMINATE
3
4
FLOCCULATION
RAPID
MIX NO.1
5
SEDIMENTATION
CHLORINE
AFTER 4/76
FLUORIDE
POLYPHOSPHATE
6
POSTCHLORINATION
ANTHRAFILT
GRAVITY
FILTERS
CO_2
RECARBONATION
7
TO STORAGE
AND CITY
250,000
GALLONS
CLEAR WELL

from various locations within the distribution system and both chlorine residual and total coliforms were determined on these samples. No adverse effects were noted. The obvious benefits of this change resulted in the permanent relocation of the chlorine dose.

TABLE 5. TRIHALOMETHANE FORMATION AFTER RELOCATION OF THE PRECHLORINATION DOSE

Sampling Date	pH	Concentration in Clear Well	
		$CHCl_3$, µg/l	$CHCl_2Br$, µg/l
4/28/76	7.9	35	4
5/4/76	8.0	40	12
5/14/76	9.1	58	6
5/20/76	9.2	99	11
5/26/76	9.2	69	4

Monitoring

Additional monitoring of the system was carried out for 2 months following the relocation of the prechlorine dose. Samples were collected from Stations No. 1, 3, 5, 6 and 7. A portion of the sample from Station 3 was chlorinated with sodium hypochlorite, designated as sample 3a, and treated identical to the samples collected from other stations. This sample was used to approximate the concentrations of trihalomethanes which would have been formed in the treatment process if the prechlorination step had not been moved.

Samples from Sta. 5 were adjusted to pH 7 (redesignated as 5a) and hypochlorite was added. This sample represented the trihalomethanes formed at a near neutral pH. It was not feasible to operate the treatment plant at this pH for reasons of water stability. This will be more fully discussed later.

Table 6 shows the median values for chloroform and bromodichloromethane from a set of 12 samples collected during June and July. Throughout this period only chloroform and bromodichloromethane were detected of the six organic parameters considered. The mean percent reduction for chloroform during this period was 75%, but the effluent bromodichloromethane concentration actually was higher than anticipated. It appears that the bromodichloromethane forms at a slower rate (compare Stations 3a, 6, and 7). This is not the complete story, however, as in 10 of the 12 samples tested, the bromo-

dichloromethane concentration is higher at Sta. 5a than at Sta. 3a. This phenomenon is more noticeable later in the report and will be discussed in more detail at that time.

TABLE 6. MEDIAN TRIHALOMETHANES DURING MONITORING PERIOD

Station	Median $CHCl_3$, µg/l	Median $CHCl_2Br$, µg/l
1	a	a
3	a	a
3a	230	2
5a	30	6
6	32	1
7	57	9

a. Below detection limit of 0.1 µg/l.

Figure 3 shows the actual chloroform delivered to the distribution system (Sta. 7) when compared to the potential chloroform which would have been given to the consumer if the prechlorination dose had not been moved from after presedimentation to the recarbonation basin (See Figure 2). The mean chloroform concentration was 222 µg/l for samples collected at Sta. 3 and adjusted by hypochlorite addition (Sample 3a). Mean chloroform found in the clear well during this period was 59 µg/l. The reduction obtained was approximately 75%.

The results obtained at Sta. 6 are compared to Sta. 7 in Figure 4. Samples from Sta. 7 were used to obtain the chloroform concentrations contributed to the distribution system, while the samples from Sta. 6 can be used to illustrate the portion furnished by the prechlorination dose. Approximately 50% of the chloroform in the plant effluent was produced by the chlorine added just prior to filtration. Although variables such as pH, temperature, reaction time, and precursor concentration could not be controlled, the authors believe that the reaction at Sta. 6 is limited by the amount of chlorine added at this location. Chlorine residuals were run on the samples after determining the trihalomethanes and were found to be zero or near zero in all cases for Sta. 6. The mean chloroform concentration at Sta. 6 was about 30 µg/l.

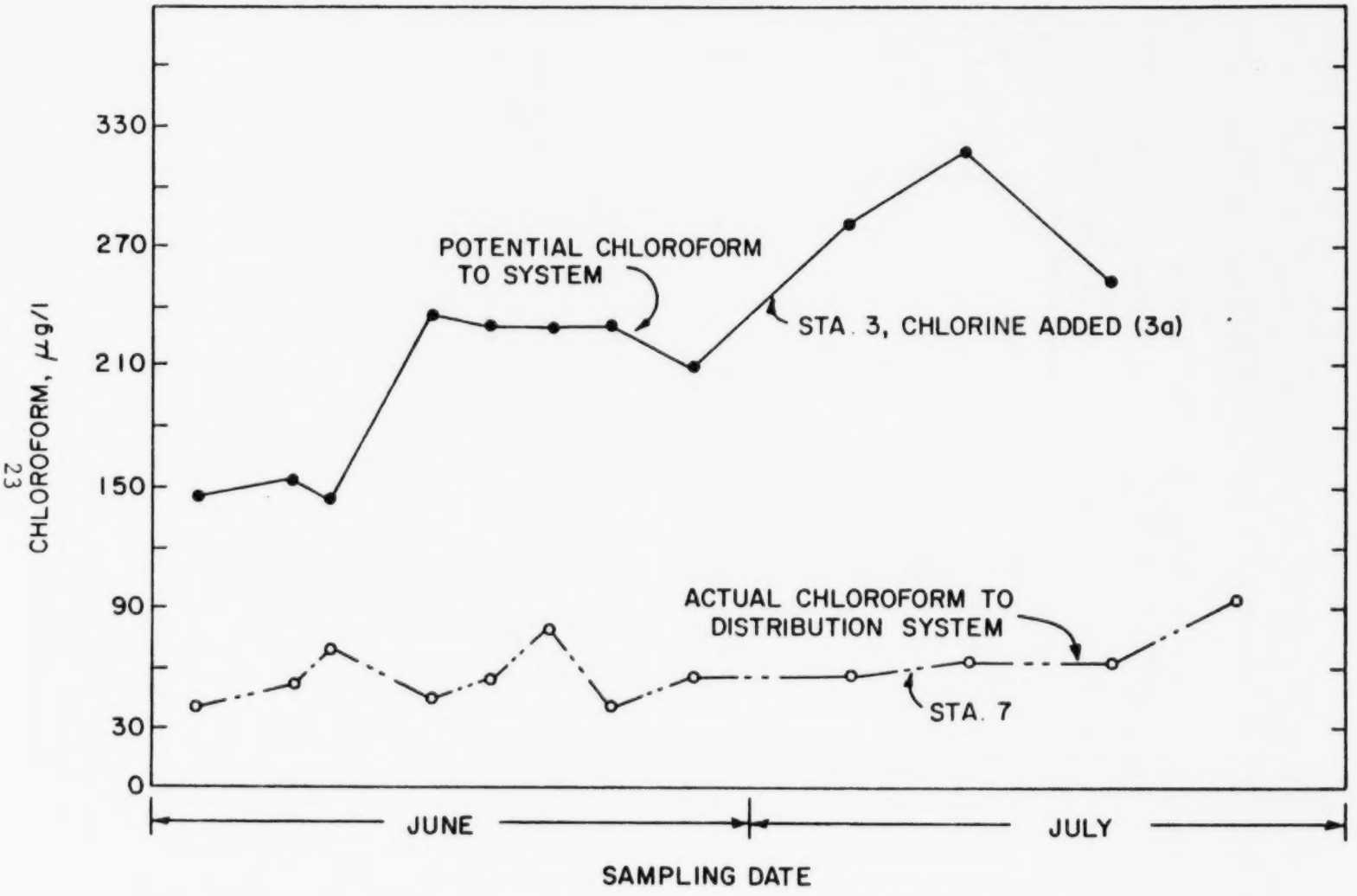


Figure 3. Potential versus actual chloroform formation after chlorination change.

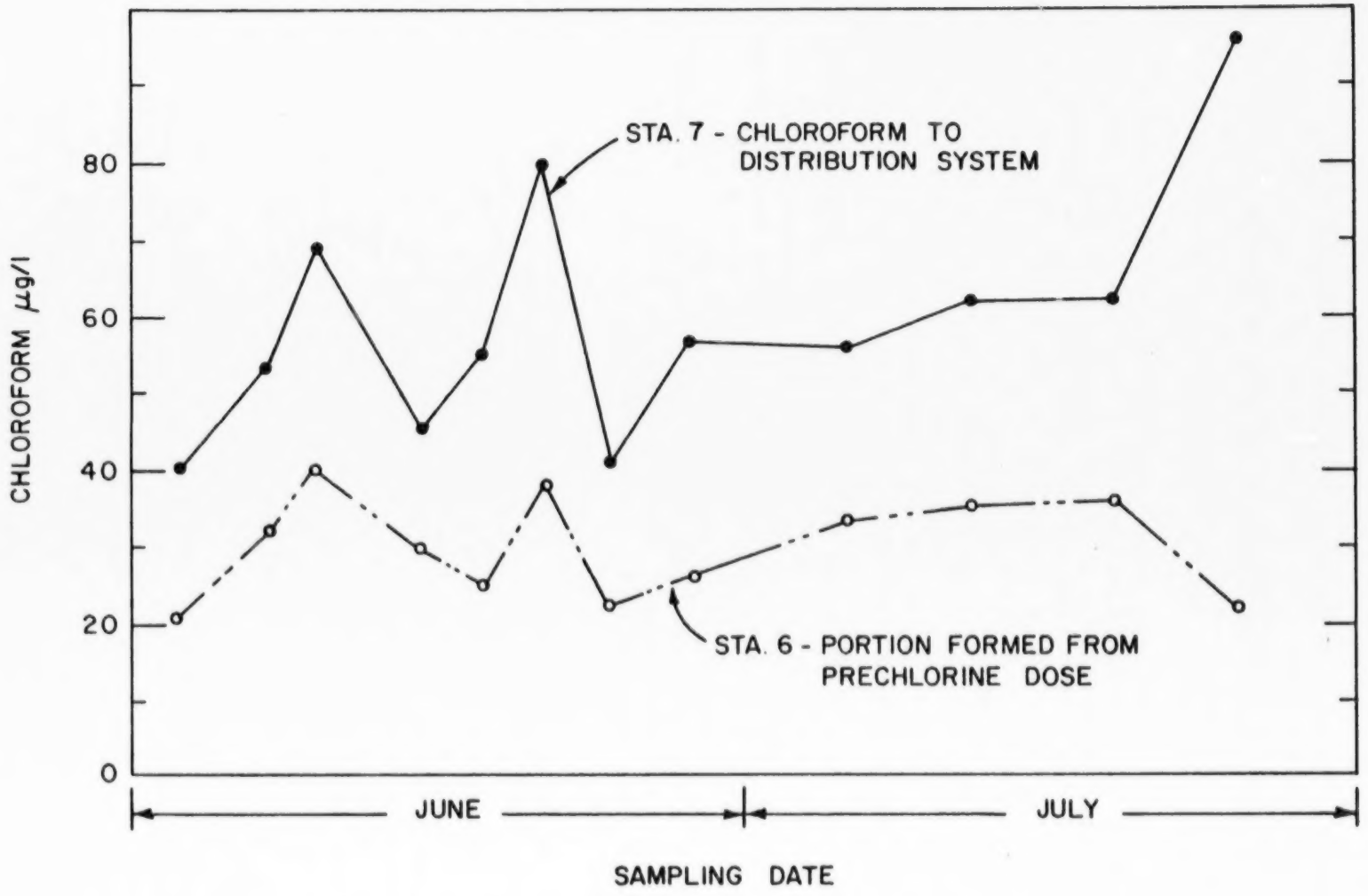


Figure 4. Portion of chloroform formed by prechlorine dose.

An interesting item to note is that prior to the relocation of the prechlorine dose, that prechlorination accounted for almost 100% of the chloroform in the plant effluent. For example on 2/10/73 the chloroform concentration at Sta. 3, just after prechlorination, was 203 µg/l (See Table 3); and the chloroform concentration in the plant effluent was 210 µg/l.

The astute reader may wonder how the present reaction at Sta. 6 could be chlorine limited when previously there was adequate chlorine available to allow for the formation of over 200 µg/l of chloroform. One of the side benefits to moving the prechlorine dose was a reduction in the amount of chlorine used. For example, initially chlorine was added on 9/8/75 at a dose rate of 6.8 mg/l for the prechlorine dose and 2.6 mg/l for the postchlorination step. On 6/2/76 these same two rates were 1.6 mg/l and 2.9 mg/l, respectively. Thus, there was a 76% reduction in the amount of chlorine available to react with precursors during the prechlorination stage.

Figures 5 and 6 show the general trends for bromodichloromethane during the monitoring period. Comments on Figure 6 which compares the concentration of bromodichloromethane at Sta. 6 with Sta. 7 would seem to be generally the same as those given for Figure 4, i.e., that the reaction at Sta. 6 is chlorine limited and that the concentration at Sta. 6 represents the portion of the final bromodichloromethane discharged to the distribution system. However when the combined data on both figures are compared, the answers do not appear to be simple ones.

For example, Figure 5 which compares concentrations of bromodichloromethane at Sta. 3a and Sta. 7 gives some interesting results. The effluent concentration is much higher than that formed at the intermediate sampling station. The samples from Sta. 3 were artificially chlorinated with sodium hypochlorite while the on-stream samples from Sta. 7 were chlorinated with chlorine gas. This should not be a factor, however, because elemental chlorine is almost completely hydrolyzed to HOCl and OCl^- at a very rapid rate (9). It is known that the bromodichloromethane reaction proceeds slowly for several days (8), but the difference in detention time would be only a few hours and would not appear to be an explanation.

Original dibromochloromethane concentrations in the plant effluent were in the 15 to 42 µg/l range. The values for Sta. 7 in Figure 5 do not reveal a substantial reduction for this constituent as a result of moving the prechlorination dose. It has been documented that both temperature and pH affect the haloform concentrations (4) (14). The major factor within the plant at Huron seems to be one of pH adjustment and is the reason for the results stated. A discussion of pH effects follows.

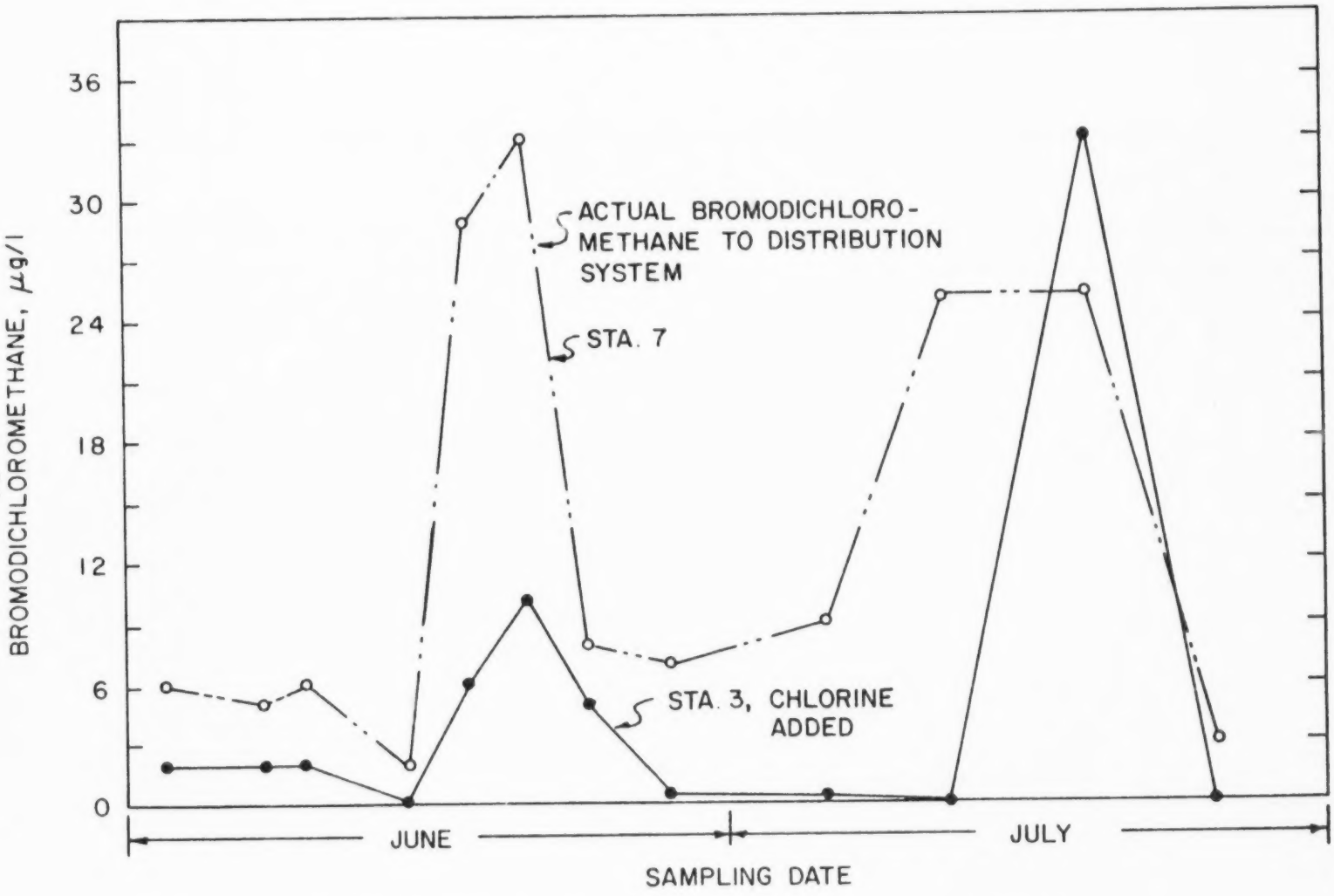


Figure 5. Bromodichloromethane formation after chlorination change.

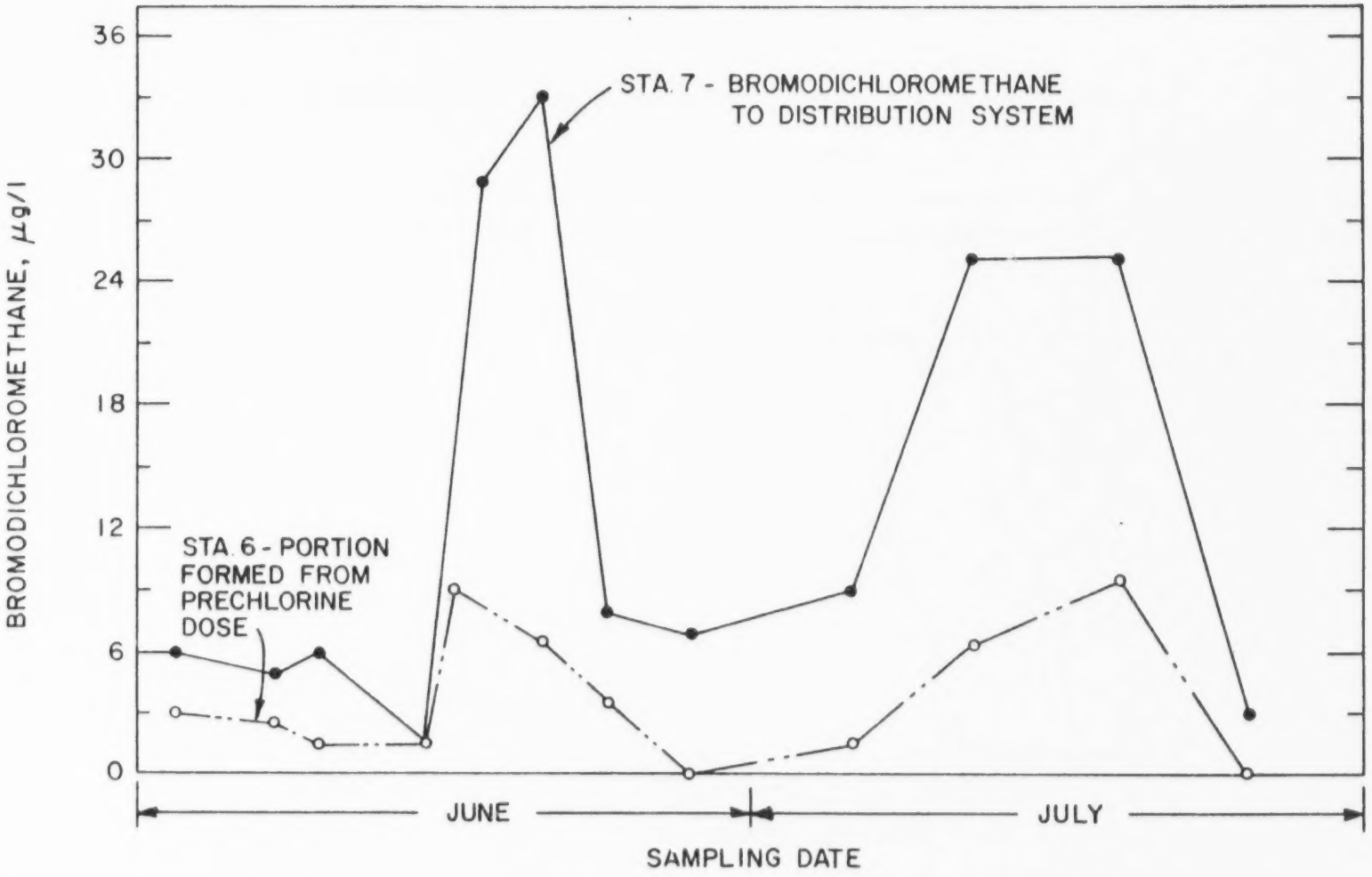


Figure 6. Portion of bromodichloromethane formed by prechlorine dose.

pH Effects

The influence of pH on chloroform concentration was documented by J. J. Rook in a laboratory study (4). His data showed a significant increase in chloroform concentration between pH 7 and pH 10, with the rate of increase becoming very rapid at the higher pH value. Similar conclusions can be drawn from the data shown in Figure 7. These data were collected from a full-scale treatment process. The points scatter somewhat about the regression line, but several critical parameters such as temperature, chlorine dose rate, precursor concentration, and detention time were not controlled, as would be expected in a field investigation of this type.

These data indicate that a chloroform concentration of only about 40 µg/l would be formed if the water was recarbonated to a pH of 7 before chlorination. If other variables were under control in the field, it might be possible to lower the effluent concentration of chloroform to approximately 20 µg/l (See the dashed line, Figure 7 which eliminates the points of widest scatter). This speculation is confirmed by the data shown in Figure 8. Samples were taken from Sta. 5 (after sedimentation) and chlorinated after the pH had been adjusted to 7. As seen in the graph, the chloroform formed was about 20 to 40 µg/l which substantiates the previous data given in Figure 7. Efforts to reduce the plant effluent to a lower pH are reported in the section on water stability. The initial sample at Sta. 5 had a chloroform concentration of 90 µg/l which seems much too high when compared with the remaining data. All the samples were grab samples so some fluctuations were to be expected, but this particular value should be viewed with suspicion.

It has been noted in a previous section that a substantial reduction was not obtained in bromodichloromethane concentrations by relocating the prechlorination dose. The primary reason for gaining the reduction in chloroform concentration was the effect of pH on this concentration, as discussed above. Figure 9 shows a plot of the bromodichloromethane concentrations in the clear well against the pH of the clear well. From the scatter of the data points, it is obvious that pH has a minor affect on the bromodichloromethane concentration. Thus, changing the location of the prechlorination dose did not substantially affect the concentration of this constituent.

Temperature Effects

Although the effect of temperature on chloroform for-

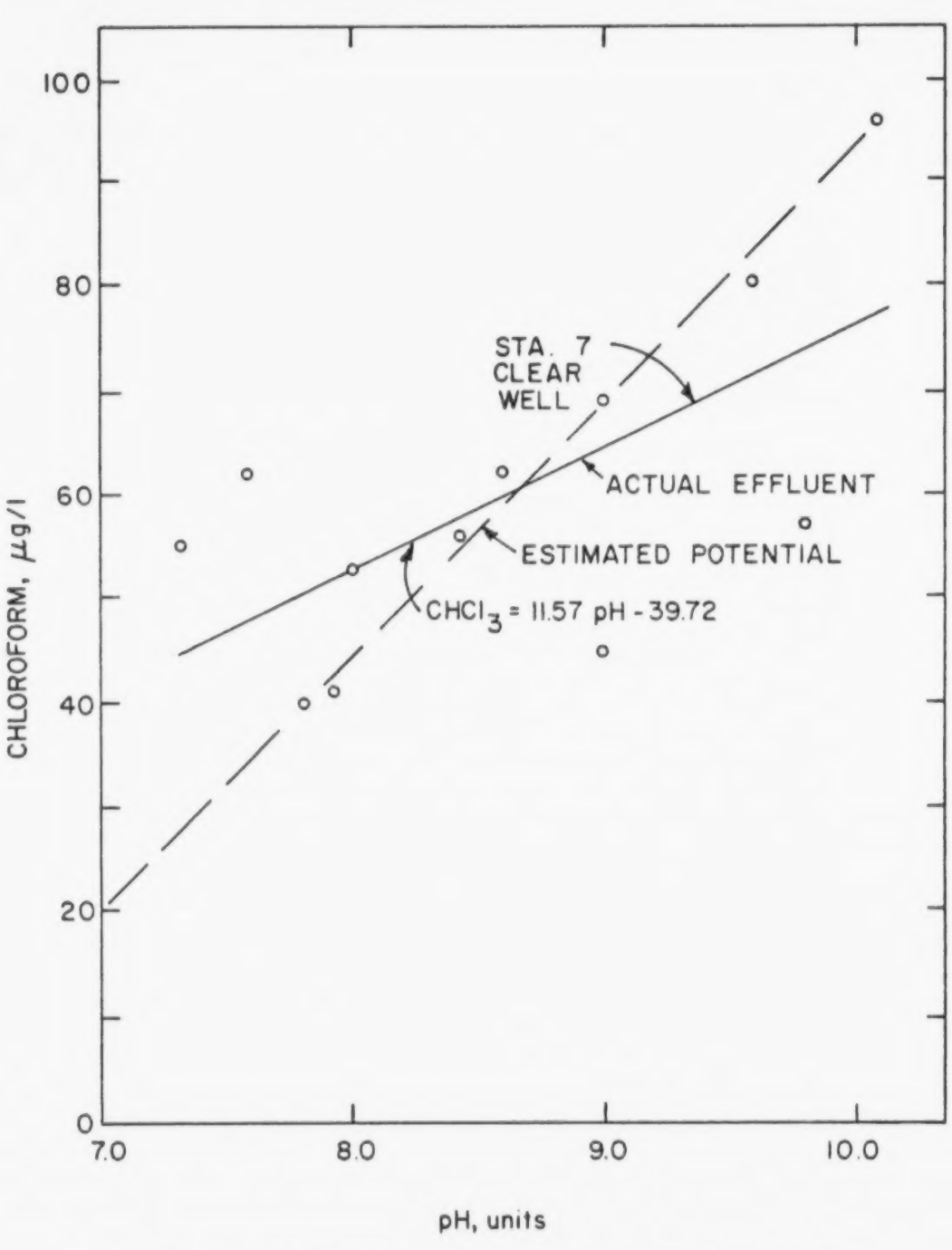


Figure 7. Effects of pH on chloroform formation.

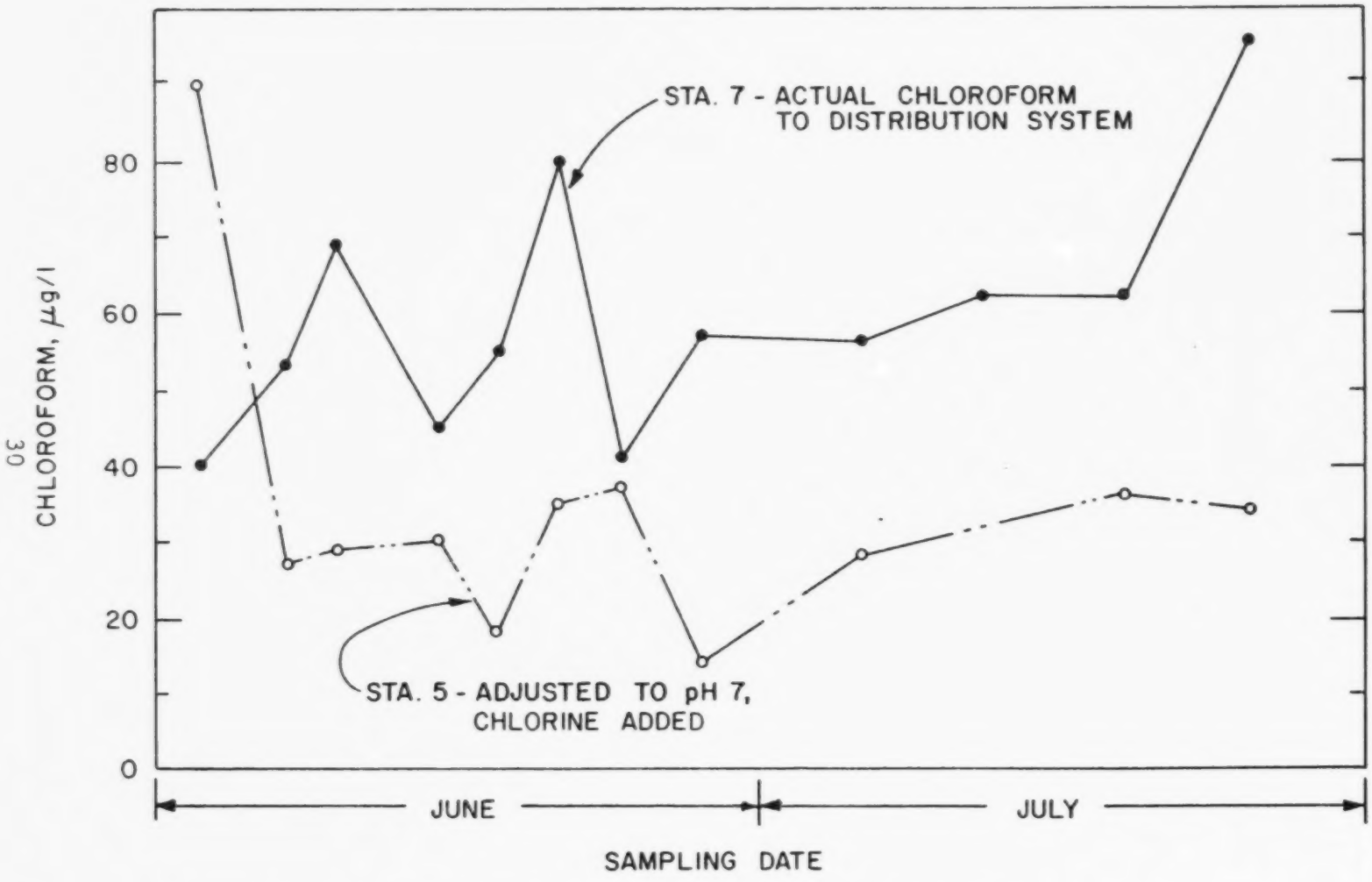


Figure 8. Chloroform reduction by lowering effluent pH.

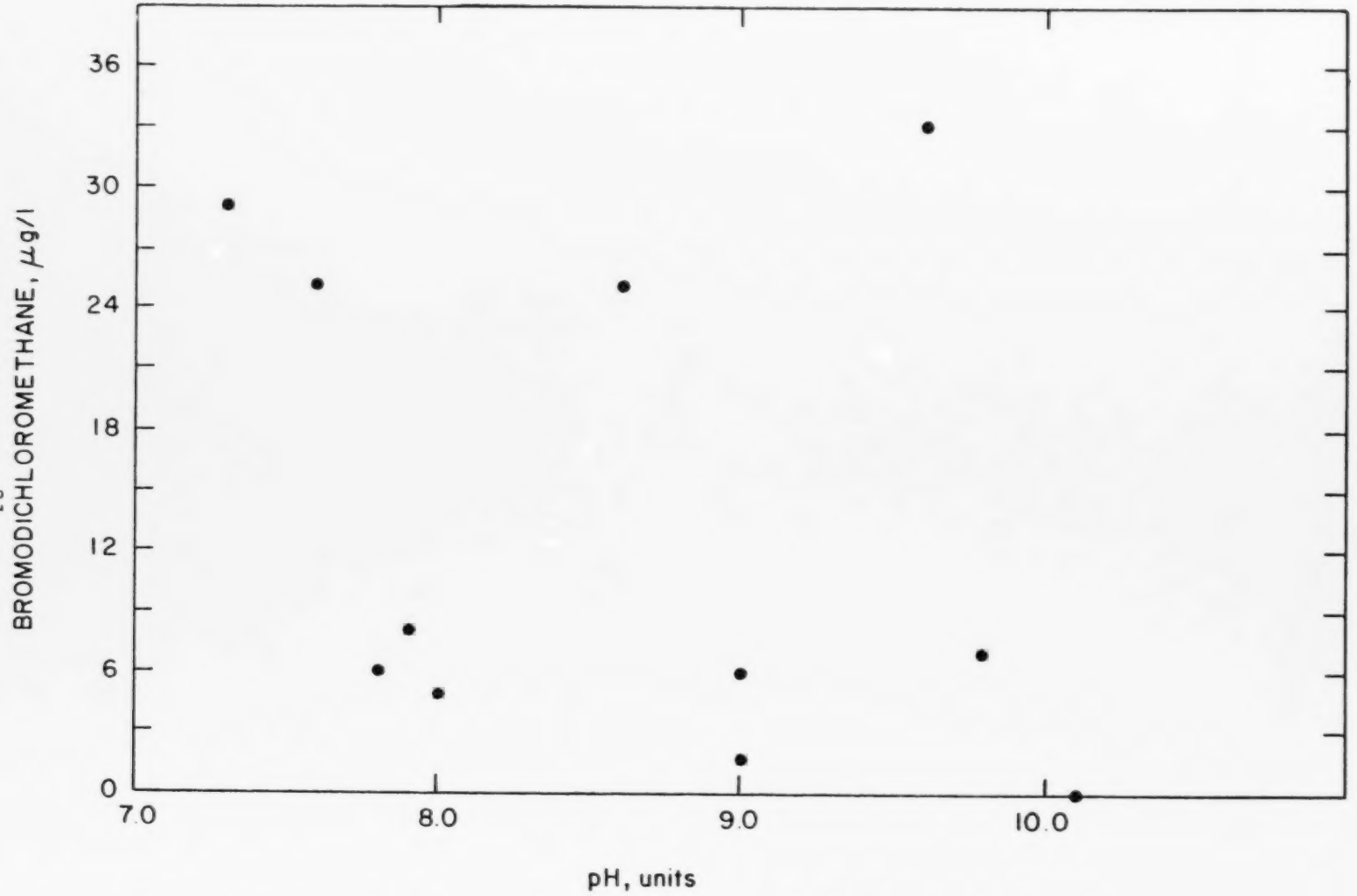


Figure 9. Bromodichloromethane relationship to pH in clear well.

mationhas been documented (14), no noticeable temperature effect was shown at the Huron Water Treatment Plant. Temperature was a minor variable during the monitoring period, and the temperature changes were probably masked by other variables such as pH and precursor concentrations. The following table gives temperature, and chloroform and bromodichloromethane values for Sta. 6 (clear well) during June. No correlation with temperature is noted.

TABLE 7. TEMPERATURE AND HALOFORM VARIATIONS AT STA. 7 DURING JUNE

Date	Temperature, °C	$CHCl_3$, µg/l	$CHBrCl_2$, µg/l
6/1/76	20.5	40	6
6/7/76	23.0	53	5
6/9/76	25.0	69	9
6/14/76	23.0	45	<2
6/17/76	20.0	55	29
6/20/76	21.0	80	33
6/23/76	21.0	41	8
6/27/76	21.5	57	7

Stability Studies

The information previously presented regarding pH effects indicates that it would be desirable to have the effluent pH near 7, because pH 7 appears optimum for chloroform control. However, the water treatment process used at Huron uses lime for softening. Good treatment practices dictate that the lime softened water be recarbonated so that a thin film of calcium carbonate is deposited in the distribution system pipe network. The thin layer of scale is useful in retarding corrosion and helps prevent "red water" complaints.

Stability control of the finished water at Huron is based on several years of good experience using the Ryznar Stability Index (15). This index gives a pH of approximately 9 for the lime softened water. Reducing the finished pH to a lower value to prevent chloroform formation would result in an aggressive or corrosive water. This, of course, would not

be acceptable.

Originally when recarbonation was used to lower the pH of a water after softening, the idea was to convert all the remaining carbonates to bicarbonates. Final pH would then be about 8.3. Actual practice soon found that a water thus treated was aggressive, not stable. Investigation of this problem was made using the Langelier Saturation Index, the Ryznar Stability Index, and the well known marble test. The conclusion was that the final effluent as currently produced at Huron was stable and that the pH of the final effluent should not be lowered unless the softening process was altered.

The main problem with lime softened water is the low alkalinity remaining after softening, and the tendency for this water to dissolve scale and precipitates in an attempt to increase the alkalinity. Several bench scale softening experiments were conducted in an attempt to use soda ash with or without lime to leave a higher alkalinity while still obtaining a soft water for the consumer. Presently the raw water at Huron is such that only lime is required to produce a satisfactorily softened water. No satisfactory results which could be recommended for full-scale application were forthcoming from the softening experiments, and these studies were abandoned.

Future changes in the raw water quality at Huron might be cause for reconsideration of the chemical dosages for softening. The raw water quality at Huron during the period of this study is given in Table 8. The interested reader is referred to other selected readings for a more detailed coverage of this problem (16) (17) (18) (19).

TABLE 8. RAW WATER QUALITY AT HURON, SOUTH DAKOTA

Date	Total Hardness, mg/1 $CaCO_3$	Calcium Hardness, mg/1 $CaCO_3$	Total Alkalinity, mg/1 $CaCO_3$	pH
9/15/75	224	136	256	8.6
12/11/75	252	140	240	7.9
3/15/76	420*	232	360	7.4
5/12/76	260	112	228	8.3
5/30/76	232	120	180	8.1
6/3/76	232	156	220	7.8

*Maximum hardness observed in one year's records

Variations in the Distribution System

The National Organics Reconnaissance Survey (1) examined

raw and finished waters of 80 cities and did not inspect changes which may have occurred within the distribution system. For the most part, the study reported herein did likewise. The initial work was heavily concentrated on the haloform formations which took place within the treatment process. Samples were not dechlorinated on site, and it was assumed that the values for Sta. 7 (clear well) represented about the concentrations which were delivered to the consumer.

The data presented in Table 9 were obtained from the stations given below on samples that were dechlorinated in the field with potassium ferrocyanide because the use of sodium thiosulfate is thought to interfere with haloform determinations (21). It can be seen that the concentrations within the distribution system are not synonymous with those of Sta. 7.

Sta. 7 - Clear well at water treatment plant, not dechlorinated in the field.

Sta. 8 - Masonic Building in downtown Huron, medium residence time.

Sta. 9 - Riverside Park near water plant, short residence time.

Sta. 10- Airport near dead end in distribution system, long residence time.

TABLE 9. HALOFORMS WITHIN THE DISTRIBUTION SYSTEM

Date	Station	$CHCl_3$, µg/l	$CHCl_2Br$, µg/l
7/5/76	7	56	9
	8	99	24
	9	122	24
	10	128	29
7/11/76	7	62	25
	8	106	38
	9	152	43
	10	153	37
7/18/76	7	62	25
	8	140	57
	9	115	44
	10	146	47
7/25/76	7	96	0
	8	142	48
	9	79	22
	10	118	29

This data in Table 9 indicate that the concentrations of the haloforms fluctuate in the distribution system, and they are higher than recorded at the plant effluent. This is important because it is the concentration at the tap which is the cause for concern. Residence time in the distribution system is not the entire answer, and a host of factors such as precursor level, temperature, effluent pH, and available chlorine need to be evaluated. This is a significant problem that requires additional study.

Operating Experience

The foregoing information documents the advantages gained by relocating the prechlorination dose. This section of the report reflects on the plant operation after the chlorine was repositioned, April to December 1976.

It was previously mentioned that the prechlorination dose was primarily used to lengthen the filter runs between washings. Referring to Figure 1, the relocated pre-chlorine dose remained prior to the gravity filters. To date (December 1976), the operating personnel at the treatment plant have not had to shorten the filter runs.

One might also suspect an increase in taste and odor problems from biological growths in the now unchlorinated portion of the plant. This problem has not been experienced at Huron. However, those considering similar chlorination revisions at other water works facilities should consider the possibility of taste and odor problems. Softening is practiced at the Huron treatment plant and the resulting high pH discourages most biological metabolism.

Of obvious interest is a comparison of chlorine usage before and after changing the point of chlorine application. Table 10 gives the average chlorinator settings for both the prechlorinator and the postchlorinator from April through December of 1975 and 1976. The 1976 data represents chlorine used after the point of chlorine application was changed, while the 1975 data are for comparison only. It is not possible to draw exact comparisons because the quality of the raw water was variable. However, general trends should be noted. During 1975 the majority of the chlorine was added from the prechlorinator, and the postchlorine dose was about 1/3 of the prechlorine dose. However, during 1976, the prechlorine dose was reduced by almost 75% and the postchlorine dose had to be increased to maintain an adequate residual.

TABLE 10. EFFECTS OF CHLORINATION REVISIONS ON CHLORINE DOSE

Month	Average Chlorinator Setting, lb /day			
	Prechlorinator		Postchlorinator	
	1975	1976	1975	1976
April	150	50	20	70
May	200	60	60	90
June	240	70	80	150
July	410	90	160	210
August	350	80	150	210
September	250	70	100	180
October	210	60	60	160
November	180	50	50	110
December	110	50	30	90

Table 11 gives some indication of the savings obtained from the in-plant chlorine adjustments. Average results are a monthly savings of $215 (equivalent to one ton of chlorine per month), a savings of about $2.08 per million gallons processed. Again it should be remembered that these are approximate comparisons because of the variations in the raw water quality. Specifically the water became very difficult to treat after July of 1976 because there was not any flow in the James River. Additional planks were added to the 3rd Street Dam to create a stagnant pool of river water from which the Huron Water Treatment Plant withdrew its raw water.

Disinfection with Chloramines

It has been shown that it is the free chlorine that reacts to form the haloforms during chlorination. Also, the use of chloramines is known to result in a lower chloroform concentration than would be produced using conventional chlorination procedures (13). What is not known is the disinfecting capabilities of the chloramines under field operating circumstances. Some data exist which doubt the effectiveness of this agent (20).

Preliminary studies of some bench-scale experiments using chloramines gave favorable results. Only low levels of both chloroform and bromodichloromethane were detected. The results are preliminary in nature as difficulties with the test were encountered and disinfection was not considered, but the process definitely warrants further study.

TABLE 11. SAVINGS FROM CHLORINE REVISIONS

Month	Water Processed, Million Gallons/Month		Total Chlorine Used lb/month		Average Cl_2 Dose, mg/l		Net Savings,*	
	1975	1976	1975	1976	1975	1976	$Mo.	$/MG
April	54.785	59.953	3038	2077	6.65	4.15	103.31	2.24
May	66.666	92.577	5075	3162	9.13	4.10	205.65	4.51
June	82.160	127.403	6349	5253	9.27	4.95	117.82	3.87
July	140.945	124.658	13,671	7094	11.63	6.82	707.03	4.31
August	96.165	78.116	9877	5519	12.32	8.47	468.49	7.60
September	73.478	73.448	6216	4494	10.14	7.34	185.12	2.52
October	68.807	58.732	4539	3279	7.91	6.69	135.45	1.10
November	47.861	46.765	2626	2241	6.58	5.75	41.39	0.75
December	47.585	45.780	1966	2237	4.95	5.86	(-29.13)	(-.81)
						Average	215.01	2.90

*Based on Chlorine @ $215/Ton

SECTION 8

FUTURE WORK

Additional work at the Huron water works should be done to further reduce the levels of haloforms delivered to the consumer. It is believed by the authors that the more fruitful approach is to attempt to prevent the halogenated hydrocarbons from forming, as opposed to the removal of these compounds after they have been formed. Possible procedures could include:

1. Correlation of the raw water quality with the trihalomethane formation in the treatment plant. Data would need to be collected during runoff events, and in general the surface supply should be monitored for organic material, solids, turbidity, and possibly some specific precursors.

2. Additional investigate work on the distribution system. It needs to be established whether the increase in haloform concentrations within the system is a time dependent problem or if additional precursors are added after the water leaves the treatment plant.

3. Using chlorine dioxide for disinfection. Chlorine dioxide is formed by onsite generation using sodium chlorite.

$$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$$

The apparent advantage to the use of chlorine dioxide is that it does not react with the same materials in water that chlorine does and measurable amounts of trihalomethane are not produced. It also leaves a residual to be measured, an advantage over ozone. A disadvantage is the additional generating equipment needed. The existing V-notch chlorinator can be used to feed the chlorine, but a chlorine dioxide generator and pump would need to be purchased. Another disadvantage is that ClO_2 is easily removed from solution in open vessels. This

may cause some problems in the point of application. Also, the gas is extremely explosive (22). There is some question regarding the toxicity of the chlorite formed by the reduction of ClO_2 (23). This hazard would need to be more fully evaluated before application to a full scale treatment process.

4. Ammonia addition. If ammonia is added along with chlorine in the proper amounts, a combined chlorine residual will result. The combined residual is not as reactive as free chlorine residuals with respect to trihalomethane formation. An ammoniator would be required for in-plant use, and the process would need to be carefully monitored to be sure that free residual chlorine was not formed in order to keep trihalomethane formation to a minimum. Some initial laboratory work to quantify the disinfection capabilities of combined chlorine residual would probably also be necessary, as well as microbiological monitoring in the field.

SECTION 9

REFERENCES

1. "Preliminary Assessment of Suspected Carcinogens in Drinking Water - Report to Congress." U.S. Environmental Protection Agency, Washington, D.C. (Dec. 1975).

2. "Report on Water Supply System and Proposed Improvements for City of Huron, S.Dak." J. T. Banner and Assoc., Inc., Brookings, S.Dak. (May 1975).

3. Symons, J. M., et al., "National Organics Reconnaissance Survey for Halogenated Organics." Jour. Amer. Water Works Assn., 67, 634 (1975).

4. Rook, J. J., "Haloforms in Drinking Water." Jour. American Water Works Assn., 68, 168 (1976).

5. Bellar, T. A., et al., "The Occurrence of Organohalides in Chlorinated Drinking Waters", Jour. Amer. Water Works Assn., 66, 703 (1974).

6. Baker, R. A., and Malo, B. A., "Water Quality Characterization-Trace Organics." Jour. San. Eng. Div. Proc. Amer. Soc. Civil Engr., 93, 41 (Dec. 1967).

7. Bellar, T. A., and Lichtenberg, J. J., "Determing Volatile Organics at Microgram per Litre Levels by Gas Chromatography", Jour. Amer. Water Works Assn., 66, 703 (1974).

8. Kinssinger, L. D., and Fritz, J. S., "Analytical Notes-Analysis of Drinking Water for Haloforms." Jour. Amer. Water Works Assn., 68, 435 (1976).

9. Morris, J. C., and McKay, G., "Formation of Halogenated Organics by Chlorination of Water Supplies." Office of Research and Development, US EPA, Washington, D.C. (March 1975).

10. Love, O. T., et al., "Preliminary Results of Pilot Plants to Remove Water Contaminants" in "Preliminary Assessment of Suspected Carcinogens in Drinking Water, Interim Report to Congress." USEPA, Washington, D.C. (June 1975).

11. Morris, R. L., and Johnson, L. G., "Agricultural Runoff as a Source of Halomethanes in Drinking Water." Jour. Amer. Water Works Assn., 68, 492 (1976).

12. "EPA Proposal on Control Options for Organic Chemical Contaminants." Federal Register, 41, 28991 (July 14, 1976).

13. Symons, J. M., et al., "Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes." Municipal Environmental Research Laboratory, USEPA, Cincinnati, Ohio (June 1976).

14. Stevens, A. A., et al., "Chlorination of Organics in Drinking Water." Jour. Amer. Water Works Assn., 68, 615 (1976).

15. Ryznar, J. W., "A New Index for Determining Amount of Calcium Carbonate Scale Formed by a Water." Jour. Amer. Water Works Assn., 36 (April 1944).

16. Langelier, W. F., "Chemical Equilibria in Water Treatment." Jour. Amer. Water Works Assn., 38, 169 (1946).

17. Larson, T. E., "The Ideal Lime-Softened Water." Jour. Amer. Water Works Assn., 43, 649 (1951).

18. Hoover, C. P., "Stabilization of Lime-softened Water." Jour. Amer. Water Works Assn., 34, 1425 (1972).

19. Larson, T. E., "Corrosion by Domestic Waters." Bul. No. 59, Illinois State Water Survey, Urbana (1975).

20. Kruse, C. W., et al., "The Enhancement of Viral Inactivation by Halogens." Water and Sewage Works, 118, 187 (June 1971).

21. Kopfler, F. C., et al., "GC/MS Determination of Valatiles for the National Organics Reconnaissance Survey (NORS) on Drinking Water." In "Identification and Analysis of Organic Pollutants in Water," Ann Arbor Sci. Pub. Inc., Ann Arbor, Mi. (1975).

22. White, G. C., "Handbook of Chlorination." Van Nostrand Reinhold Co., New York, N. Y. (1972).

23. Myhrstad, J. A., and Samdal, J. E., "Behavior and Determination of Chlorine Dioxide." Jour. Amer. Water Works Assn., 61, 205 (1969).

SECTION 10

APPENDIX

Haloform Data

TABLE A1. Haloform Data

Date	Parameter*	Sampling Station 1	2	3	4	5	6	7
2/10/76	$CHCl_3$	ND	5	203	208	215	175	210
	$CHBrCl_2$	ND	ND	22	14	10	35	42
2/23/76	$CHCl_3$	ND	8	180	175			
	$CHBrCl_2$	ND	ND	13	6			
3/2/76	$CHCl_3$	ND	ND	3		8		111
	$CHBrCl_2$	ND	ND	ND		ND	15	
3/18/76	$CHCl_3$	ND				ND	18	73
	$CHBrCl_2$	ND				ND		
3/24/76	$CHCl_3$	ND		ND		ND	5	25
	$CHBrCl_2$	ND		ND		ND	<1	10
4/28/76	$CHCl_3$	ND	ND				27	35
	$CHBrCl_2$	ND	ND				2	8
5/4/76	$CHCl_3$	ND	ND				26	40
	$CHBrCl_2$	ND	ND				4	12
5/14/76	$CHCl_3$	ND	ND				20	58
	$CHBrCl_2$	ND	ND				ND	2
5/20/76	$CHCl_3$	Sampling error						99
	$CHBrCl_2$							11
5/26/76	$CHCl_3$	6	4				8	69
	$CHBrCl_2$	ND	ND				1	4

TABLE A1. Continued.

Date	Parameter*	Sampling Station 1	3	3a	5a	6	7
6/1/76	$CHCl_3$	9	5	144	90	21	40
	$CHBrCl_2$	ND	ND	2	6	3	6
6/7/76	$CHCl_3$	ND	ND	152	27	32	53
	$CHBrCl_2$	ND	ND	<2	4	2	5
6/9/76	$CHCl_3$	ND	<1	144	29	40	69
	$CHBrCl_2$	ND	ND	ND	<2	<2	6
6/14/76	$CHCl_3$	ND	ND	235	30	30	45
	$CHBrCl_2$	ND	ND	ND	<2	<2	<2
6/17/76	$CHCl_3$	ND	<1	230	18	25	55
	$CHBrCl_2$	ND	ND	6	10	9	29
6/20/76	$CHCl_3$	ND	1	230	35	38	80
	$CHBrCl_2$	ND	ND	10	9	7	33
6/23/76	$CHCl_3$	ND	<1	230	37	22	41
	$CHBrCl_2$	ND	ND	5	8	4	8
6/27/76	$CHCl_3$	ND	ND	210	14	26	57
	$CHBrCl_2$	ND	ND	<1	2	ND	7

TABLE A1. Continued.

Date	Parameter*	Sampling Station 1	3	3a	5a	6	7	8	9	10
7/5/76	$CHCl_3$	ND	ND	288	28	33	56	99	122	128
	$CHBrCl_2$	ND	ND	<1	6	<2	9	24	24	29
7/11/76	$CHCl_3$	ND	ND	316	-	35	62	106	152	153
	$CHBrCl_2$	ND	ND	ND		7	25	38	43	37
7/18/76	$CHCl_3$	ND	ND	264	36	36	62	140	115	146
	$CHBrCl_2$	ND	ND	33	15	10	25	57	44	47
7/25/76	$CHCl_3$	ND	ND	-	34	22	96	142	79	118
	$CHBrCl_2$	ND	ND	ND	6	ND	ND	48	22	29

*All values given in µg/l
ND = Not Detectable